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<td>作者</td>
<td>井口 裕介</td>
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<tr>
<td>発行日</td>
<td>2010-03-25</td>
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<td>URL</td>
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PhD Dissertation

Gravity-induced diffusion of atoms
in some semiconductor materials

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Graduate School of Science and Technology
Department of Pulsed Power Science, New Frontier Science
Kumamoto University

March, 2010
### Contents

Subject: Gravity-induced diffusion of atoms in some semiconductor materials

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>..............................................(4-16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td></td>
</tr>
<tr>
<td>1-1.</td>
<td>Introduction  ..................................5</td>
</tr>
<tr>
<td>1-2.</td>
<td>Previous studies ................................7</td>
</tr>
<tr>
<td>1-2-1.</td>
<td>Theoretical studies ...........................7</td>
</tr>
<tr>
<td>1-2-2.</td>
<td>Experimental study 1 (Sedimentation of atoms in solid Bi-Sb) 8</td>
</tr>
<tr>
<td>1-2-3.</td>
<td>Experimental study 2 (Sedimentation of atom in solid Se-Te)  9</td>
</tr>
<tr>
<td>1-3.</td>
<td>Purpose of the present study ..................11</td>
</tr>
<tr>
<td>1-4.</td>
<td>Summary .........................................12</td>
</tr>
<tr>
<td>References</td>
<td>................................................................13</td>
</tr>
<tr>
<td>Figures</td>
<td>................................................................14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>..............................................(17-34)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>New high-temperature ultracentrifuge at Kumamoto University</td>
</tr>
<tr>
<td>2-1.</td>
<td>Introduction  ..................................18</td>
</tr>
<tr>
<td>2-2.</td>
<td>Apparatus  .......................................19</td>
</tr>
<tr>
<td>2-3.</td>
<td>Performance and specifications ................21</td>
</tr>
<tr>
<td>2-4.</td>
<td>Summary ..........................................23</td>
</tr>
<tr>
<td>References</td>
<td>................................................................24</td>
</tr>
<tr>
<td>Figures</td>
<td>................................................................25</td>
</tr>
</tbody>
</table>

APPENDIX (The operating manual for ultracentrifuge apparatus) ..........................33

<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>..............................................(35-48)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystalline change of Bi-Sb alloy under a strong gravitational field</td>
</tr>
<tr>
<td>3-1.</td>
<td>Introduction  ..................................36</td>
</tr>
<tr>
<td>3-2.</td>
<td>Properties of Bi-Sb ............................36</td>
</tr>
<tr>
<td>3-3.</td>
<td>Experimental conditions .......................37</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>3-4</td>
<td>Results and discussion</td>
</tr>
<tr>
<td>3-4-1</td>
<td>Grain refinement</td>
</tr>
<tr>
<td>3-4-2</td>
<td>Deformation twinning</td>
</tr>
<tr>
<td>3-4-3</td>
<td>Homogeneously composition structure</td>
</tr>
<tr>
<td>3-5</td>
<td>Summary</td>
</tr>
<tr>
<td>References</td>
<td></td>
</tr>
<tr>
<td>Figures</td>
<td></td>
</tr>
</tbody>
</table>

Chapter 4  
Sedimentation of isotope atoms in monoatomic Se  
(Aim for sedimentation of isotopes)

4-1. Introduction  .................................................................50
4-2. Properties of selenium ..................................................50
4-3. Experimental conditions ...............................................51
4-4 Results and discussion ..................................................52
  4-4-1. Centrifuge at Solid phase .........................................52
  4-4-2. Centrifuge at Liquid phase .......................................53
4-5 Summary .............................................................................56
References ..............................................................................57
Figures ....................................................................................58

Chapter 5  
Sedimentation of impurity atoms in InSb semiconductor  
(Aim for sedimentation of atom and Impurity control)

5-1. Introduction .................................................................65
5-2. Properties of In-Sb ........................................................65
5-3. Experimental procedure ...............................................66
  5-3-1. Sample preparation ..................................................66
  5-3-2. Measurement method ...............................................67
  5-3-3. Van der Pauw measurement .......................................67
5-4 Results and discussion ..................................................69
  5-4-1. Centrifuge with Ge impurity thin film ..........................69
  5-4-2. Centrifuge with impurity thin film of transition metals ....70
  5-4-3. Centrifuge only InSb single crystal ............................71
Chapter 6  

Interface structure control of a-Si:Ge multi layer thin film
under a strong gravitational field
(Aim for Control of Interface)

6-1. Introduction   .................................................-83
6-2. Preparation of a-Si:Ge multi thin film   .................................................-83
6-3. Experimental procedure   .................................................-84
6-4 Results and Discussion    .................................................-86
   6-4-1. SAX(Small angle incident X ray) measurement   .................-86
   6-4-2. SNMS(Secondary Neutron Mass Spectroscope)measurement ......-88
6-5 Summary   .................................................-89
References   .................................................-90
Figures   .................................................-91

Chapter 7  

Conclusion

7-1. Summary of this dissertation   .................................................-101

ACKNOWLEDGEMENTS   .................................................-103
Chapter 1

Preface
1-1. Introduction

Research under microgravity field has been used in many fields, and still these have kept high activities as symbolized ISS (International Space Station) and Kibo. Materials science research using strong gravitational field up to 1 million G (1 G = 9.8 m/s²) is still an unexploited area. Under strong gravitational field, each atom is displaced by a one-dimensional body force. A strong gravitational field also realized the sedimentation of atoms in solid, i.e. an atomic-scale graded structure, and so on [1,2]. And until now, a strong gravitational field has been researched for the sedimentation of large composition gradient. It is very interesting not only large gradient happen, but also impurity control, interface control, condensation of isotope and others so on.

To start the research of the strong gravitational field (1,000,000 G in maximum), T. Mashimo et al. developed an ultracentrifuge in 1996 [1] on the basis of self consistent theory for the sedimentation of atoms in condensed system reported in 1988 and 1994 [2,3]. This apparatus was combustion turbine type and could generate a gravity of over 1,000,000 G for long duration and high temperature around 100-250 °C. And the sedimentation of substitutional solute atoms were achieved on the binary Bi-Sb alloy system using this apparatus [4,5].

After this report, another ultracentrifuge experiments and new machine development have been performed many times, mainly mechanical problems for strength of rotor, capsule, and turbine motor, heating unit, measurement method of temperature, lubricants and others. After then, the new ultracentrifuge (2nd generation apparatus) which is compressed air turbine type and be able to generate a strong gravitational field up to over 1,000,000 G in a wide temperature range around 80-400 °C with high stability controls was developed in 1999 by Mashimo et al. The variety experiment could be start in higher melting point material and phenomena using this ultracentrifuge. And in 2006, this new ultracentrifuge (2nd generation, compressed air turbine type) was developed at Kumamoto University. This is able to generate a strong gravitational field up to over 1,000,000G, too, and temperature range is 200-550 °C. Now we try to continue improvement that we can operate under room temperature.

In this study, we researched about the application for condensation of isotope, impurity control, crystalline control and interface control under a strong gravitational field using the ultracentrifuge of Kumamoto University and JAEA. At first, new ultracentrifuge is explained. After then new experimental results and
mechanism will be discuss. There is already known that graded composition structure was achieved by under a strong gravitational field due to the sedimentation of atoms in solid, but all of mechanism is unclear. In this report, these problems be discussed and considered with hypothesis and settlement.
1-2. Previous studies
1-2-1. Theoretical studies

Almost all sedimentation phenomena of both macroscopic solutes and atoms or molecules have been analyzed using the Lamm (1929) sedimentation equation [8] or similar equations (Miller 1956 [9], Brenner and Condiff 1972 [10]), which were formulated for axially symmetric macroscopic particles on the basis of macroscopic mechanics and thermodynamics. In these theories, the self-interaction effect between macroscopic solutes caused by centrifugal field are not considered, therefore, the driving body force is not expressed as a function of solute concentration. In previous studies on liquid solvents (Archibald 1947 [11], Van Holde and Baldwin 1958 [12], Block et al. 1977[13]), the density was either assumed to be constant or else experimentally determined. The sedimentation phenomena of atoms in solid have been similarly analyzed (Barr and Smith 1969 [14], Anthony 1970 [15], Rushbrook and Barr 1978 [16]). However, if the constituting particles are atoms or molecules, the density of the mixture solvent changes with concentration, even if it is under higher solute concentration. Therefore Lamm’s theory is not strictly applicable to such sedimentations.

Prof. T. Mashimo has proposed self consistent equations for the sedimentation of atoms in a multi-component condensed system in 1988, 1994 [2,3]. We would like to introduce these equations in this chapter. The theory was constructed on the basis of the mean-field approximation, the linear phenomenological matrix law with an expression for the atom fluxes and the Nernst-Einstein relations. Accordingly, the effects of self-interaction between the solutes, density changes and chemical activities, etc…were consistently taken into account. Steady state solutions of the sedimentation of atoms were obtained under centrifugal field in 2 or 3 component system under several atomic and chemical conditions in the infinite energy region. Using this theory, we can simulate the sedimentation process without additional assumptions or experimental data, even for finite regions. We would like to introduce the simulation procedure in this chapter, shortly.
1-2-2. Experimental study 1 (Sedimentation of atoms in solid Bi-Sb)

To start the study of the sedimentation of atoms in solid under a strong gravitational field, T. Mashimo et al., our laboratory, developed an ultracentrifuge apparatus which is the combustion gas turbine type in 1996 [1]. The apparatus can generate an acceleration field of over \(1 \times 10^6\) G for long time duration at high temperature. The specifications of it are showed in the Chapter 3. Using this apparatus, they formed atomic-scale graded structures by the sedimentation of component atoms in an all proportional miscible system of Bi\(_{70}\)Sb\(_{30}\) (mol\%) binary alloy at bulk body in 1997[4,5]. The experimental conditions were shown in Table 1-1.

Continuous composition gradient of Sb (about 20-0 wt\%) and Bi (about 80-100 wt\%) were observed in the centrifuged sample by EPMA measurement (Figure 1-1(a)). Also, the continuous changes in the lattice constants were observed by X-ray diffraction measurement. These results show that an atomic-scale graded structure was formed by the sedimentation of atoms in all-proportional miscible alloy under a strong gravitational field of 1,000,000 G (1 million G) in maximum acceleration at high temperature. It must be noted that the substitutional solutes with rate of component level acted in the sedimentation of this system, while interstitial solutes (Au) at rate of impurity level acted in some elemental metals with low melting temperature in the report of others [14,15,16]. In addition, crystal growth into the direction of gravity was also observed (Figure 1-1(b)). It is expected that the sedimentation of substitutional atoms can be used to control the compositions and crystalline structure of alloy and compounds.
1-2-3. **Experimental study 2 (Sedimentation of atom in solid Se-Te)**

Some atomic-scale graded structures were already formed in some alloys by sedimentation of substitutional solute atoms. However, these alloys only show a metallic bond, and the sedimentations in the alloys or compounds with other bonds, such as covalent bond, ionic bond, and molecular bond, are still unknown. A large linearly graded structure on atomic scale up to 88 at%/mm with oriented grown crystals was formed in Selenium-Tellurium semiconductor using a strong gravitational field [17]. Se-Te system is an allproportion miscible system. The bonding between neighboring atoms in the same chain is covalent and the bonding between atoms belonging to neighboring chains seems to be intermediate between the metallic bond and the Van der Waals contact. Se and Te are direct-band gap semiconductors. The Se-Te solid solutions show the semiconductor properties in all compositions and the band gap increases monotonically with Se concentration in Se-Te solid solution. This is motivated by the possibility to control the band gap energy and the lattice constant through the control in composition on the atomic scale. The band gap engineering allows for the design of new light emitters-detectors operating in a desired spectral range of electromagnetic radiation. In this study, we performed the strong gravitational field experiment as shown Table 1-2.

The polarized microscope photograph of the plate-type specimen ultracentrifuged under a strong gravitational field of 0.78 x 10^6 G at maximum acceleration at 260 °C for 90 h is shown in Figure 1-2-a), the linear composition profiles (EPMA result) of Se and Te along the direction of gravity are shown in Figure 1-2-b), and the changes in the binding energies of Se and Te 3d electrons as a function of the distance from the area with a maximum rotation radius are shown in Figure 1-2-c). The crystal growth and the change in the composition along the direction of gravity were observed for the whole specimen. The content of Te increased linearly in the direction of gravity from about 0 to 65 wt %, while the content of Se decreased linearly from about 100 to 35 wt % within a narrow region of only about 0.6 mm wide. The binding energy of Se 3d electron greatly decreased linearly from 55.1 to 54.7 eV in the direction of gravity for the whole specimen, while the binding energy of Te 3d electron slightly decreased from 573.7 to 573.6 eV. The chemical shifts might be due to the different chemical environments, which were caused by rearrangement of the charge distribution of valence electrons in the Se-Te solid solution. These results showed that the electronic state changed after
Chapter 1, Introduction of strong gravitational research

ultracentrifugation and the band structure should be also continuously changed along the direction of gravity for these specimens. Therefore, a novel large linearly atomic-scale graded semiconductor with oriented grown crystals was successfully formed using a strong gravitational field.
Chapter 1, Introduction of strong gravitational research

1-3 Purpose of the present study

In this study, we studied the application research using the ultracentrifuged process. The sedimentation of atom and atomic-scale graded composition structure in solid with all miscible alloys and compounds were already achieved, so we need to progress researches. In this report mention about “Isotope enrichment” “Impurity control” “Crystalline structure” “Control of Interface morphology”. These topics are included some phenomena of the sedimentation of atoms, but we approach to discuss much about the phenomena under a strong gravitational field and the latest industrial applications.

1) Crystalline change by a strong gravitational field
2) Sedimentation of isotope by a strong gravitational field
3) Sedimentation and control of impurity atoms in semiconductor by a strong gravitational field
4) Control of interface morphology and sharpness by a strong gravitational field
Chapter 1, Introduction of strong gravitational research

1-4 Summary

In this Chapter 1, we introduced a strong gravitational field, previous studies, and expected effect on material. In the Chapter 2, we talk about the ultracentrifuge apparatuses in Kumamoto University and Japan Atomic Energy Agency.

In the Chapter 3 to 6, we talk about each result. Chapter 3 is “Crystalline structure” research of the centrifuged Bi$_{70}$Sb$_{30}$ under small acceleration and short duration (which is compare with our usual condition, acceleration and duration is about 1/10) to observe the crystalline effect without composition changes due to the sedimentation of atoms. Chapter 4 is “Isotope enrichment” research of the centrifuged monoatomic Selenium. Chapter 5 is “Impurity control” research of the centrifuged single crystal InSb semiconductor with some impurity thin film and without any impurity elements. Chapter 6 is “Control of Interface morphology” research of the centrifuged amorphous Si-Ge multilayer thin film which is deposited by magnetron sputtering.
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Table 1-1. Experimental conditions of the previous study for Bi-Sb alloy

<table>
<thead>
<tr>
<th>Starting sample</th>
<th>Max acc. (g)</th>
<th>Temperature (°C)</th>
<th>Duration (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{70}$Sb$</em>{30}$ (at%)</td>
<td>(0.96-0.79)x10$^6$</td>
<td>220-240</td>
<td>85</td>
</tr>
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</table>

Table 1-2 Experimental conditions of the previous study for Se-Te(70:30 at%).

<table>
<thead>
<tr>
<th>Starting sample</th>
<th>Max acc. (g)</th>
<th>Temperature (°C)</th>
<th>Duration (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{70}$Te$</em>{30}$ (at%)</td>
<td>(0.78-0.77)x10$^6$</td>
<td>260</td>
<td>90</td>
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</table>
Figure 1.1 Experimental result of sedimentation in solid Bi-Sb system [5]
Figure 1.2 (a) Polarmicroscope photograph of the ultracentrifuged Se$_{70}$Te$_{30}$ plate-type specimen. (b) Linear composition profiles (c) Changes in the binding energies of Se and Te 3d electrons [17]
Chapter 2

New high-temperature ultra-centrifuge at Kumamoto University
2-1. Introduction

To study the sedimentation of atoms or crystal chemical instability in solids under a strong acceleration field, Prof. Mashimo et al. developed the combustion gas turbine type ultracentrifuge apparatus in Kumamoto University in 1996 [1] at first. The apparatus can generate an acceleration field of over 1,000,000 G for long time duration at high temperatures (<250°C). Mega gravity of $1 \times 10^6$ G on the sample is to be accomplished in the rotational speed of 219,200 rev/min with the rotor and capsule. The maximum rotational speed of the rotor have ever been recorded is 240,000 rev/min (1,200,000 G just for very short time). 225,000 rev/min (1,005,000g) is the maximum rotational speed for performing the experiment in safely for long time duration. However, the gravitational field, energy range and sample scale achieved by this apparatus were very limited, because the small rotor (46 mm in outer diameter) with center bore was used in air atmosphere by a hot air turbine motor. The temperature of sample was also limited to about 250°C due to the hot air heating method on this apparatus. In addition, the stabilities in rotational speed and temperature were not so good with the ripples of about 5% and 5°C, respectively.

And next development, a compressed air turbine type ultracentrifuge apparatus (2nd generation) in Japan Atomic Energy Agency (JAERI at that time) was produced by Mashimo et al, it could generate strong gravitational field up to over 1,000,000 g in a wide temperature range up to 400°C with high stability controls, to expand the investigation variety in materials and phenomena [2].

Recently, a new ultracentrifuge apparatus which is almost same with 2nd generation apparatus was produced in Kumamoto University. Now a strong gravitational field around 600,000 G and >500°C can be generated in maximum, it was calculated by FEM simulation of centrifugal phenomena using new rotor and spindle made by Inconel 718.
2-2. Apparatus

The schematic layout of the new ultracentrifuge apparatus is shown in Figure 2-1. The setup mainly consists of an air turbine motor, a sample rotor, a vacuum chamber and a controller. The air turbine motor provided by Maruwa Electronic Inc. consists of two 32 mm-diameter turbine wheels made of aluminum alloy, a spindle made of stainless steel or Inconel 718, and two ceramic ball bearings. Two turbine wheels are driven by compressed air (up to 6.5 kg/cm²) supplied by a screw compressor through an electromagnetic air control valve allowing the air flow to be precisely controlled. By changing the torques for two turbine wheels which can be driven at opposite direction each other, the rotational speed can be precisely controlled, but now we do not be equipped breaking unit, yet. The dumper section is set at the down side of the turbine wheels to suppress the vibration of rotor for high stability. And we equipped the induction heater. We can control the experimental temperature to use this heater.

Figure 2-2 shows a schematic around the dumper section and rotor. The dumper section consists of two dumper bushings (upper and lower bushings). The upper one is constructed by the inner (1) and outer (2) bushings (double structure) made of different kinds of metals to decrease the friction velocities of the bushing with the spindle and dumper for the further high speed rotation, as shown in Fig. 2-2. The rotor chamber is vacuumed by a rotary pump to less than several tens Pa. The turbine motor and the rotor are connected by a 4.78mm-diameter spindle, and are separated by an oil seal made of rubber, which support vacuum in the chamber. The rotational speed and the vibration are measured by an electromagnetic pickup. The motor is capable of rotating the rotor with a diameter up to 140 mm to a rotational speed up to 165,000 rpm in a vacuum, but the rotational speed is limited mainly by the strength of the rotor. The present apparatus is equipped with safety circuits.

Figure 2-3 shows a photograph of the rotor with an outer diameter of 80 mm and sample capsules and schematic of cross section. The rotor has not a center bore, but has a shallow hole for setting at the spindle by using screws. We can raise the maximum rotational speed or the scale of rotor, because the ultracentrifuge-induced stresses generated in non-bored rotor are remarkably smaller than those in bored rotor. The rotor is made of titanium alloy (Ti-6A1-4V) which is up to 350°C and iron-nickel alloy (Inconel 718) which is up to 520°C for the experiments, respectively. Sample capsules of six or eight with an inner diameter of
5 mm and a depth of about 20 mm inserted at 30° from the spindle axis at symmetrical sides of the rotor as shown Fig 2-3.

The dynamic balancing of the rotor is carefully set up within a residual unbalance value of 0.1g mm. The rotor can be heated by an induction heating in a vacuum. The radiation wall made of carbon graphite with an inner diameter of 160 mm is heated by induction heating to achieve the rotor temperature for up to about 700°C without rotation. The rotor temperature is measured by K type thermo couples. At first, we have to measure the heating condition without rotation, and logged temperature condition of inside of graphite wall, sample and some points. After then we decide the heating condition of centrifugal experiment.

Figure 2-4 shows an example of the temperature control data [4] (temperatures of the sample, and the part where very near from rotor of the inner carbon wall), when the rotor was stopped, and the final setting temperature of the sample was 400°C. The temperatures of the rotor and further the sample followed it, and the one of the sample finally reached to the setting temperature (400°C) at about 2 hour. In this experiment, we confirmed that the rotor could be heated to >400°C using a carbon graphite radiation wall and thermal insulator wall combined with the induction heating, as shown in figure 2-4. Figure 2-5 shows the photographs of a) the main part, and b) rotor which set into the turbine, c) the heater unit. There is heat control set ups for experiment of the present apparatus.
2-3. Performance and specifications

Ultracentrifuge experiments were performed to determine the performance of the present apparatus by using an 80 mm-diameter rotor made of titanium alloy [4,5], we did not perform the details of rotation specification in Kumamoto University because it is almost same setup with JAENA's one. Figure 2-6 shows the 1st spin test data at Kumamoto University (rotational speed and vibration) of a short-time and ultracentrifuge experiment (160,000 rpm), where the maximum gravitational field at sample was 1,000,000 G at 35.6 mm in radius. X axis is time (seconds), Y axis of left is vibration of spindle with rotor and Y axis of right is rotation speed per minutes. The vibration value of the rotor was 20 µm (now it is smaller than this case, about 10 µm for 100 hours). The rotational speed and the sample temperature were remarkably stable with the ripples of <0.05 % and <1°C, respectively. Now, the high-temperature and long-time ultracentrifuge experiments by using the 80mm-diameter rotors made of Inconel alloys (maximum 125,000rpm, 400°C, 100 hours, respectively), where the maximum acceleration field were about 600,000 G, respectively, were also successfully performed in Kumamoto University. Figure 2-8 shows the recent experiment data for 100,000 rpm (about 400,000G), 400°C, 60 hours, respectively. The red line is rotation speed, the blue line is calibrated sample temperature and green line is vibration of spindle with rotor. X axis is time (hours), Y axis of left is rotation speed of 1x10^-1 rpm and Y axis of right is temperature (°C) and vibration of 1x10^1 µm.

It is important to raise sample temperature for the expansion of investigated variety of materials and phenomena. In order to realize large composition change of element or isotope by sedimentation of atoms in solids or liquids, we necessitate a large value of potential energy rather than gravitational field. The final composition profiles are represented as a function of the difference in potential energy between atoms (\(\Delta E = \Delta M r^2 \omega^2/2RT\) \(\Delta M\), R, T, \(\omega\) and \(r\) are the difference in atomic weight, the gas constant, absolute temperature, angular rate and radius, respectively) according to the self-consistent theory of the sedimentation of atoms in condensed matter[2, 3].

The maximum potential energy achieved by the present apparatus increased by a factor of even >2 compared with that of the Kumamoto University's old combustion gas turbine type [1]. The sample volume also increased by a factor of >4 compared with the combustion gas turbine type. The comparison of the performance between the apparatuses of the combustion gas turbine type and the
new air turbine type is summarized in Table 2-1.

The maximum gravitational field can be increased more by improvement of the design and material of rotor, etc. The sample temperature can be increased to >500°C by the induction heating. The potential energy and sample volume can be also increased by the factors of larger than 3 and 10, respectively, compared with those of the combustion gas turbine type by using the rotor with a diameter of >80 mm.

We are now adding a cooling system by a radiation cooling and gas blow cooling method with this apparatus. It is expected that the investigation materials for proteins and phenomena under a strong gravitational field will be expanded much by using the present apparatus.
2-4. Summary

In this chapter, we mentioned about the specification of new ultracentrifuge and centrifugal experiment. Ultracentrifugal experiments could be succeeded with the very stable rotation at high temperature.

1) New ultracentrifuge (2nd generation apparatus) was started up at Kumamoto University.
2) New ultracentrifuge can achieve more stable rotation and higher temperature than old combustion gas turbine type ultracentrifuge.
References

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   http://reposit.lib.kumamoto-u.ac.jp/handle/2298/440
Table 2-1 Comparison of the performance between the ultracentrifuge apparatuses

<table>
<thead>
<tr>
<th>apparatus</th>
<th>Diameter of rotor (mm)</th>
<th>sample size (mm)</th>
<th>Max. Max. Acc.</th>
<th>sample temperature (° C)</th>
<th>potential energy</th>
</tr>
</thead>
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<tr>
<td>gas combustion type</td>
<td>46</td>
<td>3mm diameter</td>
<td>220,000</td>
<td>1,000,000</td>
<td>80–250</td>
</tr>
<tr>
<td>air turbine type (present)</td>
<td>80–160</td>
<td>&gt;5mm diameter</td>
<td>165,000</td>
<td>&gt;1,000,000</td>
<td>0–520</td>
</tr>
</tbody>
</table>
Figure 2-1: Photograph and schematic layout of the new ultracentrifuge which is compressed air turbine type.
Figure 2-2 the schematic around the dumper section and rotor.
Chapter 2, New high-temperature ultra centrifuge at Kumamoto University

Figure 2-3 Photograph of the rotor with an outer diameter of 80 mm and sample capsules and schematic of cross section.
Figure 2.4 Temperature control data of the sample position measured by K type thermocouples with bulk Aluminum and Brass. These were heated by the induction heater and setting temperature of sample is 400°C.
Chapter 2, New high-temperature ultra-centrifuge at Kumamoto University

a) Main part

b) Rotor which is set into the turbine

c) A induction heater which set in apparatus

Figure 2-5 Photographs of the experimental set up.
Figure 2-6 The 1st spin test data at Kumamoto University (rotational speed and vibration) of a short-time and ultracentrifuge experiment (160,000 rpm), where the maximum gravitational field at sample was 1,000,000 G at 35.6 mm in radius.
Figure 2.7: The ultracentrifugal experiment data for 100,000 rpm (about 400,000G), 400°C, 60 hours, respectively. And average vibration is about 12 μm during the strong gravitational experiment.
APPENDIX

The operating manual for ultracentrifuge apparatus

a) Heating test without rotation

We have capsules with fixed samples of Aluminum and Brass which have a φ1.6mm hole for sheathed K type thermocouple. These capsules were called dummy capsules. These thermocouples were set at each position as shown below Figure. The rotor, capsules and bussing section were set to turbine. Two of thermocouple 1 was set at dummy capsules into a hole of Aluminum and Brass. Thermocouple 2 was set at inner carbon wall where very near position with rotor. And we have another thermocouple (φ3.2mm) which is connected to the induction heater directly, at inside of carbon wall.

After finish these set up, we set the almost same condition with spin test. (the turbine was set to chamber. And vacuum switch and lubricant oil switch is on.) Then we can start heating test, to measure the experimental temperature like Fig. 2-4. Empirically, lower control limit is around 200°C, and upper limit is 500°C during centrifugal test due to nonnegligible the friction with air and strength of rotor.
Chapter 2, New high-temperature ultra centrifuge at Kumamoto University

b) Preparation of centrifugal experiment
- Clearance of spindle and polished busing section were set around 20µm
- Remove the unbalances of assembled rotor with capsules within 10mg
- The spindle connect to rotor and revise the error of centering within 10µm
- The rotor (with spindle) set into the turbine motor and fix using Aluminum nut.

c) Starting the ultracentrifugal experiment
- Start to rotate up to the target rpm (30000rpm and 125000rpm is dangerous due to the sympathetic vibration)
- Start to heat up to the target temperature (by induction heating)
- Start to count the duration when temperature reaches to target
- Stop the induction heater when the experimented duration finished
- Stop the rotation when the temperature of rotor was cooled enough

**Set up**
1. Set the specimen into the rotor
2. Revise the unbalance of the rotor
3. Assemble the rotor and the spindle
4. Revise the unbalance of assembly
5. Set into the turbine motor

**Start the rotation**
1. Start to rotate up to the target rpm
2. Start to heat up to the target temperature (by high-frequency induction heating)
3. Start to count the duration when temperature reaches to target
Chapter 3

Grain refinement and deformation twinning on Bi-Sb all-proportional miscible alloy
(Aim for Crystalline structure and Composition structure)
Chapter 3, Grain refinement and deformation twinning on Bi-Sb

3-1. Introduction

Materials science research using ultra-strong gravitational fields of up to 1,000,000 G (1 G = 9.8 m/s²) is still mostly unexplored. Under a strong gravitational field, heavy atoms are forced toward the gravitational direction while light atoms are forced to the opposite direction. As a result, unique crystal states with one-dimensional atom displacement and one-dimensional strain can be realized while the lattice uniformly shrinks under high pressure. A strong gravitational field also results in the sedimentation of atoms in a solid, i.e. a resultant atomic-scale graded structure in the solid etc. [1,2].

Using ultracentrifugal apparatus [3,4], atomic-scale graded structure materials were produced in a Bi-Sb alloy [5,6] and others [7,8] by the sedimentation of substitutional solute atoms, and the sedimentation of isotopes in a monometallic element was also achieved [9,10]. In addition, grain refinement was observed under a strong gravitational field [11] but the required conditions and the mechanism were unknown. In this study, some strong gravitational field experiments performed under a comparatively low gravitational field and for short durations on a Bi-Sb alloy to examine the change of crystalline state caused by one-dimensional strain and to discuss the resultant grain refinement.

3-2. The Properties of Bi-Sb system alloy

Bi and Sb lumps of 5N and 3N purity were provided by the Rare Metallic Co., Ltd. The Bi-Sb (70:30 at%) alloy samples were prepared by melting at about 350 ºC for 30 minutes and were cooled for several hours in a PYREX tube of 5 or 3 mm (inner diameter) under vacuum. The rod-shaped sample was sliced into plate-shaped disks. This type of composition sample has a semi-metallic character [12]. Bi-Sb system is all-proportional miscible system, crystal structure is rhonbohedral.
3-3. Experimental conditions

Sample 1 was prepared using a rod-type capsule. A hot-air turbine motor type centrifuge (Kumamoto University [1,3] as shown Fig. 3-1-a) was used for sample 1. The temperature for the experiments in this report was 240 °C while the duration and acceleration were 10 hours and 0.18–0.14×10⁶ G, respectively. Figure 3-1-b) shows the rotor, capsules and sample that were used. The rod-type capsules were made of SUS304. The sample from the rod-type capsule is formed by plastic deformation and stress concentration because of its asymmetric shape. The initial samples were placed in these capsules and fixed onto a Ti alloy rotor. Table 1 shows a summary of the strong gravitational field experiments.

A compositional analysis was carried out using an electron probe microanalyzer (EPMA), JXA-800R (Japan Electron Optics Laboratories Co., Ltd.). Electron backscatter diffraction pattern analysis (EBSD) was carried out to map the crystal orientation and to determine the misorientation of adjoined crystals using FE-SEM: S-4100 (Hitachi, Ltd.) and EBSD equipment (TexSEM Laboratories, Inc.).
3-4 Results and Discussion

3-4-1 Grain refinement

Figure 3-2 shows a polarized microscope photograph and the EPMA results for the sample ultracentrifuged about $0.18 \times 10^6$ G at maximum acceleration and at 240 °C for 10 hours. A compositional change was not observed. This indicates that atom sedimentation had not occurred in this experiment. We did, however, observe the graded composition structure due to the sedimentation of atoms in the sample ultracentrifuged at $1.02 \times 10^6$ G and 260 °C for 100 hours [11]. For the gravity region at $0.17 \times 10^6$ G, many small crystal grains of < 30 µm were observed. We estimate that the minimum gravitational field required for grain refinement to occur is about $0.17 \times 10^6$ G at 240 °C and 10 hours.

The difference in the body force acting on Bi and Sb atoms at $0.17 \times 10^6$ G is estimated to be $2.4 \times 10^{-19}$ N per atomic bond by the shearing force and this is due to the difference in atomic mass. The strength of the near-liquid state at around $0.8 \times T_m$ is much smaller than that at room temperature by a factor of $< 1/100$, generally. This is called the zero strength temperature (ZST). There is carbon iron as a notorious instance at near solid state [18]. It was assumed that many defects such as dislocations and vacancies can appear due to the large body force by a strong gravitational field [19]. Nucleation in the form of primary recrystallization might occur to allow for recovery from lattice strain. Therefore, many small crystals might appear. In this study, an incubation period was necessary to allow for nucleation and we determined that the incubation period for Bi$_{70}$Sb$_{30}$ is less than 10 hours under a strong gravitational field. Grain sizes were less than 30-40 µm in diameter despite the different durations probably because of repetitive nucleation and crystal growth.
3.4-2. Deformation twinning

Figure 3-3 shows the enlarged polarized microscope photographs at the points of a, b, c and d where the gravitational field values are 0.175×10⁶ G, 0.165×10⁶ G, 0.16×10⁶ G and 0.145×10⁶ G, respectively. In the area where the gravitational field was smaller than < 0.17×10⁶ G, many deformation twins were observed. As shown in the figure, a stronger gravitational acceleration leads to a thicker twinning width. The thickest width was about 100 µm. It has been reported that the deformation twinning width is small and uniform on ferrite [13,14] and on a Bi-Sb single crystal after dynamic indentation [15]. The difference in width might be due to the long treatment in the ultracentrifuge as dynamic processes such as indentation or shock compression are usually very short.

Figure 3-4 shows the EBSD map of sample 1 that was ultracentrifuged at about 0.16×10⁶ G. The width of the twins is about 10~5 µm. Table 2 shows the c-axis misorientation of each adjoining crystal and this is indicated in Fig. 3. All the misorientations were about 92 degrees. According to an investigation of the rhombohedral deformation twining of calcite (CaCO₃) [16], (1 0 -1 4 ) twinning has c-axis misorientations of 90 degrees. This result is similar to our finding for Bi₇₀Sb₃₀ and the twinning plane may be (1 0 -1 3) twinning because of misorientation and the lattice parameter. Calcite has a slip plane for deformation twinning and the slip plane of Bi-Sb in this study coincides with that of calcite. M. H. Johnston et al. reported the deformation twinning of Sn with nucleation by centrifuge at 3-6 G during the solidification process [17]. It is, therefore, easy to generate deformation twinning with some slip plane in Sn. They reported that only one kind of slip plane was present in Sn, so we assume that the same phenomenon occurs under centrifugation as well.
3-4-3. Homogeneously composition structure

Figure 3-5 shows the EPMA result of the Bi-Sb annealed at 240 °C for 24 hours (a), and the another sample (plate-shape) ultracentrifuged at about 0.85×10^6 G in maximum at 250 °C for 5 hours (b) by the air turbine motor type centrifuge (Kumamoto University as shown Fig. 2-2, Chapter 2) was used for sample 1. We could clearly observe dendrite structure at the annealed one, as shown Fig 3-5 (a). The dendritic structure is usually observed for the all-miscible-alloy system without rapid quenching. Contrary to annealed specimen, in spite very short duration, there are small dendritic segregations of centrifuged one, as shown Fig 3-5 (b). These results clearly show that not only the atomic weight dependence diffusion, but also the diffusion coefficient increases due to the vacancy-assist under strong gravitational field.

It is reason that this homogeneous composition structure formed that diffusivity increased much under strong gravitational field. This is consistent with above mentioned discussion at session “3-4-1. Grain refinement”. So many vacancies and defects were generated at near-liquid temperature by a strong gravitational field. These phenomena may be applied to new techniques, for example, control the defect level (impurity level) of semiconductor, metal alloys for hydrogen storage and etc...
Chapter 3, Grain refinement and deformation twinning on Bi-Sb

3-5 Summary

We found that deformation twins appear in the low-gravity region where grain refinement is not observed. Compared with conventional deformation twins, these twins were much thicker and were proportional to the gravitational field. For grain refinement, the minimum gravitational field was more than $0.17 \times 10^6$ G, at 240 °C for periods <10 hours. This report presents the first example of deformation twinning by a centrifugal process in a solid phase. Deformation twinning, formed under a strong gravitational field, has only one kind of slip plane because of a one dimensional body force. And we could observe very fast annealing effect under a strong gravitational field. We can consider that it caused by a lot of vacancy which relation of internal strain or defect for grain refinement.

1) The grain refinement condition on Bi-Sb all-miscible alloy under a strong gravitational field was understood.
2) It conditions were the minimum gravitational field was more than $0.17 \times 10^6$ G, at 240 °C for periods <10 hours.
3) The deformation twinning was observed by centrifugal treatment.
4) The fast-annealing effect was observed with homogeneously composition due to the vacancy induced diffusion.
References

Table 1. Summary of the strong gravitational field experiments for Bi-Sb.

<table>
<thead>
<tr>
<th>Sample (capsule type)</th>
<th>Max / Min acceleration in specimen (G)</th>
<th>Temperature (°C)</th>
<th>Duration (h)</th>
<th>Crystal state in the high / low G region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi_{70}Sb_{30} (Rod)</td>
<td>0.18×10^6 / 0.14×10^6</td>
<td>240</td>
<td>10</td>
<td>Grains of tens of µm /Deformation twins</td>
</tr>
</tbody>
</table>

Table 2. Summary of the misorientations for sample 1.

<table>
<thead>
<tr>
<th>Measurement point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Misorientation (deg)</td>
<td>92.5°</td>
<td>92.5°</td>
<td>91.9°</td>
<td>91.2°</td>
<td>91.9°</td>
<td>91.7°</td>
<td>92°</td>
<td>91.9°</td>
<td>91.2°</td>
</tr>
</tbody>
</table>
Chapter 3, Grain refinement and deformation twinning on Bi-Sb

Fig. 3-1. a) Photograph of the old ultracentrifuge which is combustion gas turbine type. b) the scheme of the cross section of rotor, capsules and sample.
Fig. 3.2. (a) EPMA result of the sample centrifuged about 0.18x10^6 G in maximum, 240 °C for 10 hours. (b) EPMA result of the sample centrifuged about 0.18x10^6 G in maximum, 240 °C for 10 hours.
Chapter 3. Grain refinement and deformation twinning on Bi-Sb

Fig. 3-3. the enlarged polarized microscope photographs at the points of (a), (b), (c) and (d) where the gravitational field values are $0.175 \times 10^6$ G, $0.165 \times 10^6$ G, $0.16 \times 10^6$ G and $0.145 \times 10^6$ G, respectively.
Chapter 3, Grain refinement and deformation twinning on Bi-Sb

Fig. 3-4. (a) Quality Image of the sample ultracentrifuged at about $0.16 \times 10^6$ G, 240 °C for 10 hours. (b) EBSD result of the sample ultracentrifuged at about $0.16 \times 10^6$ G, 240 °C for 10 hours.
Fig. 3-5. (a) EPMA result of starting sample with annealing, 240 °C for 24 hours. We could observe segregation with unclear grain border. (b) EPMA result of the enlarger sample (plate-shape) ultracentrifuged at about $0.85 \times 10^6$ G in maximum and 250 °C for 5 hours.
Chapter 4

Sedimentation of isotope atoms in monoatomic Se
(Aim for sedimentation of isotope)
4-1. Introduction

Gravity-induced diffusion (sedimentation) of isotope atoms is important from the point of view of separation of isotopes as well as diffusion physics. In nature, such phenomena might appear on or in massive stars. Enriched isotopes are indispensable for human society in the fields of atomic energy ($^{235}$U, $^6$Li, etc.), [1] medical treatment ($^{58}$Cr, $^{168}$Yb, etc.), [2] and may even be employed in the IT field for quantum computing ($^{29}$Si, etc.), [3] etc., while separation of isotopes has traditionally been carried out using gaseous centrifugation, gaseous diffusion and low temperature vapor separation. Until now, sedimentation of isotope atoms had not been realized in condensed matter, due to the very small differences in atomic weights and the self-diffusion processes, while sedimentation of interstitial solute atoms [4,5] and substitutional solute atoms of different elements [6-8] has been realized. In the present study ultracentrifuge experiments at high temperature were performed on elemental Selenium (Se) to examine the sedimentation of isotope atoms in solid and liquid matter.

4-2. About isotopes of Selenium

The crystal structure of Se is hexagonal, consisting of infinite chains of atoms spiraling around the c-axis. Se has many isotopes, [10] namely $^{74}$Se (0.9%), $^{76}$Se (9.0%), $^{77}$Se (7.6%), $^{78}$Se (23.5%), $^{80}$Se (49.7%), $^{82}$Se (9.2%), etc.

For chemistry, selenium is a catalyst in many chemical reactions and is widely used in various industrial and laboratory syntheses, especially organoselenium chemistry. It is also widely used in structure determination of proteins and nucleic acids by X-ray crystallography (incorporation of one or more Se atoms helps with MAD and SAD phasing.)

For manufacturing and materials use, the largest use of selenium worldwide is in glass and ceramic manufacturing, where it is used to give a red color to glasses, enamels and glazes as well as to remove color from glass by counteracting the green tint imparted by ferrous impurities. Selenium is used with bismuth in brasses to replace more toxic lead. It is also used to improve abrasion resistance in vulcanized rubbers.

For electronics, because of its photovoltaic and photoconductive properties, selenium is used in photocopying, photocells, light meters and solar cells. It was
Chapter 4, Sedimentation of isotope of Se single element

once widely used in rectifiers. These uses have mostly been replaced by silicon-based devices, or are in the process of being replaced. The most notable exception is in power DC surge protection, where the superior energy capabilities of selenium suppressors make them more desirable than metal oxide varistors. Sheets of amorphous selenium convert x-ray images to patterns of charge in xeroradiography and in solid-state, flat-panel x-ray cameras.

For photography, selenium is used in the toning of photographic prints, and it is sold as a toner by numerous photographic manufacturers including Kodak and Fotospeed. Its use intensifies and extends the tonal range of black and white photographic images as well as improving the permanence of prints. Early photographic light meters used selenium but this application is now obsolete.

4-3. Experimental conditions

An air turbine-type ultracentrifuge capable of generating a gravitational field of over $1 \times 10^6$ G (1 G=9.8 m/s²) at high temperatures up to over 500°C for a period of over 100 hours[9] was used for this study. The sample was prepared by melting 4N Se shot under an Ar atmosphere in a glass tube with an inner diameter of 5 mm. The sample was then placed in a capsule with an inner diameter of 5 mm and a length of about 15 mm. The capsule was then mounted in a titanium alloy rotor with an outer diameter of 80 mm. Isotope analyses were made with a Cameca ims-5f secondary ion mass spectrometer (SIMS).[11] Samples were sputtered with an O⁻ primary beam of 10 nA intensity resulting in a beam size of about 10 µm in diameter. The Electron Back Scattering Pattern (EBSP) experiment was made with an EBSP apparatus (TexSEM Laboratories,Inc.) combined with a shottky-type FE-SEM (S-4300SE of Hitachi Ltd.).
Chapter 4, Sedimentation of isotope of Se single element

4-4 Results and Discussion
4-4-1 Centrifuge at Solid phase

Figure 4-1 shows a polarized microscope photograph (a) and the isotope compositional ratio $^{82}\text{Se} / ^{76}\text{Se}$ (b) of the polished surface of the specimen which was ultracentrifuged at a rotational speed of 152,000 rev/min for 100 hours at 190°C, which was lower than the zero-pressure melting temperature of 222°C. The gravitational fields at the right and left edges (35.4 and 31.4 mm in radius) of the specimen were (0.916 and 0.813)$\times 10^6$ G, respectively. The specimen was divided into three regions. In the strong-gravity region (A), quite fine-grained crystals of a few tens of µm were observed as shown in the expanded microphotograph in Fig.4-1-a. In the mid-gravity region (B), large crystals with a grain size of several hundreds of µm long were observed. In the weak-gravity region (C), feather-shaped crystalline grains with widths at several µm growing along the gravitational field direction were observed. As shown in the compositional ratio $^{82}\text{Se} / ^{76}\text{Se}$ (Fig. 4-1-b), the content of $^{82}\text{Se}$ (i.e., $^{82}\text{Se} / ^{76}\text{Se}$) increased with gravity in regions B and C by >0.8%. This result showed that sedimentation of heavier isotopes had occurred. The concentration change was severe at the feather-shaped morphology region, which may be related to the diffusion process. However, only a very small composition change was observed in region A, where a rather fine-grained crystalline state was observed.

The difference in composition change between the A region and B or C region may be caused by the difference in diffusion coefficients, alike the case for sedimentation of elementary atoms in the Se-Te system alloy [7]. The melting point of Se increased with pressure by the Simon equation [11]. The pressure increased to about 163 MPa at the right-hand edge due to the effect of the gravitational force, which lead the melting temperature to about 257°C (zero-pressure melting temperature: 222°C) and decreased the diffusion coefficient. It is concluded that the sedimentation started in the lower gravity region due to the higher diffusion coefficient, and gradually proceeded through the higher gravity region. On the other side, for the Bi-Sb system alloy whose melting temperature does not change with pressure much, the sedimentation of elementary atoms first occurred at the opposite side (stronger gravity region) [5].

Figure 4-2 shows the EBSP mapping data for directions parallel and normal to that of gravity ($\parallel$gravity and $\perp$gravity) at the marked points by a, b, and c in the ultracentrifuged specimen. The colors of these mappings show the respective
crystalline orientations, which coincide with directions parallel and normal to that of gravity on the cut surface, where green or blue colors indicate crystalline orientations normal (c⊥), and the red ones indicate orientations parallel (c//), to the c-axis. In the strong-gravity region (A), fine-grained crystals with various colors were observed, showing that the crystalline orientations were random. The fine-grained crystals had appeared in the amorphous starting phase. This grain refinement may be related to the one-dimensional lattice strain caused by the differences in gravitational body force acting on isotope atoms. It is assumed that so many fine grained crystals appeared by recrystallization at everywhere due to the one-dimensional lattice strain even in monoatomic Se solid. However, in the mid-gravity region (B), green or blue-colored crystals (c⊥) were observed in the parallel direction mapping, whereas red-colored ones (c//) were rather observed in the normal direction mappings. It showed that the crystals grew along the c⊥ parallel to gravity direction. The EBSP mapping in the low-gravity region C showed that the crystalline orientations of the feather-shaped crystalline grains were similar to the region B. For Se the self-diffusion coefficient along the c⊥ direction is larger than that along the c// direction by about 5.2 times [12]. It is suggested that fine-grained crystals first appeared, and grew through sedimentation of isotopes along the c⊥ parallel to gravity direction under a strong gravitational field.

Simulation of sedimentation process was performed by using the finite difference equation [13] based on the self-consistent sedimentation equation [14,15]. We calculated the concentration change for the uniform diffusion coefficient for ideal reference system to compare with the experimental result, where the diffusion coefficient was not uniform depending on the melting temperature. Figure 4-3 shows a series of calculated concentration profiles for 82Se/76Se for an ideal gas reference system together with the experimental result. The concentration changes in each region might be almost uniform alike the cases of Bi-Sb [5], In-Pb [6], Se-Te [7], etc, in which local concentration changes of elementary atoms around grain boundaries were not observed. The gradient of the experimental profile in region A is slightly smaller than of the steady state analytical result for the uniform diffusion coefficient. By extending the duration of the ultracentrifuge experiments, the sedimentation may proceed in whole region of sample, and the slope approach or exceed the analytical result.
4-4-2. Centrifuge at Liquid phase

Figure 4-4 shows the polarized microscope photograph (a) and the compositional ratio $^{82}\text{Se}/^{76}\text{Se}$ (b) of the polished surface cut at a plane containing the rotation axis of the specimen which was ultracentrifuged at a rotation speed of 145,000 rpm for 100 hours at 300°C (liquid state). The gravitational fields at the right and left edges (35.2 and 31.2 mm in radius) of the specimen were 0.827 to 0.733x10^6 G, respectively. As shown in Fig. 4-4-b, the content of $^{82}\text{Se}$ continuously increased with gravitational field, and the total change in $^{82}\text{Se}/^{76}\text{Se}$ was larger than 3.5%. The change is seen to peak in the higher-gravity region.

Figure 4-5 shows the SEM photograph and EBSP mapping data for directions parallel and normal to that of gravity ($/\parallel$ gravity and $\bot$ gravity) at the marked rectangular region in Fig. 4-4 of the ultracentrifuged sample. Feather-shaped crystalline grains with widths at several µm along the direction of gravity were observed throughout the region as shown in Fig. 4-4-a, and Fig. 4-5. The colors of these mappings show the respective crystalline orientations which coincide with directions parallel and normal to that of gravity on the cut surface, where green and blue colors or red ones indicate crystalline orientations normal ($c/\bot$) or parallel ($c/\parallel$), to the $c$-axis, respectively. Green or blue-colored crystals were observed in the parallel (rolling) direction mapping, whereas red-colored ones were observed in the normal direction mappings. It showed that the crystals grew along the $c/\bot$ direction. This morphology might appear during the cooling process. For Se the self-diffusion coefficient along the $c/\bot$ direction is larger than that along the $c/\parallel$ direction by about 5.2 times.[12] It is suggested that atoms diffused along the $c/\bot$ in the short-range ordered hexagonal structures in liquid state, and crystals grew along the $c/\bot$ parallel to the direction of gravity during the cooling process under a strong gravitational field.

Simulation of sedimentation process was performed by using the finite difference equation [13] based on the self-consistent sedimentation equation.[14,15] Figure 4-6 shows a series of calculated concentration profiles for $^{82}\text{Se}/^{76}\text{Se}$ for an ideal gas reference system. The gradient of the experimental profile is twice that of the steady state analytical result (ideal gas system). This indicated that the sedimentation of isotope atoms was in a non-ideal system diffusion in spite of the same elements probably due to interaction between atoms, similar to the case of the sedimentation of different elemental atoms.[7,8,13] By extending the duration of the ultracentrifuge experiments, or enlarging the rotor scale, an even larger
concentration change might be achieved.
4-5 Summary

A strong gravitational field resulted in the sedimentation of isotope atoms in monoatomic solid and liquid.

In the solid state experiment, the layer crystalline morphology consisting of three zones of the fine-grained crystals, the long crystals and feather-shaped crystals grown parallel to gravity direction appeared in the specimen ultracentrifuged at 0.8-1 million G and at 190°C. Change in concentration ratio $^{82}\text{Se}/^{76}\text{Se}$ of $>0.8$ % was observed in the grown crystalline region. These results show an evidence for sedimentation of substitutional atoms in solid via self-diffusion, and suggest possibility of application to control of impurity and crystalline state as well as to isotope separation.

In the liquid state experiment, the concentration ratio $^{82}\text{Se}/^{76}\text{Se}$ increased by greater than 3.5 % in specimen ultracentrifuged at 0.7-0.9 million G and at 300°C. The recovered sample had a feather-shaped crystalline morphology. The concentration gradient was nearly twice that of the steady state analytical result (ideal gas system), indicating a non-ideal system diffusion. The present result is evidence of sedimentation of substitutional atoms in condensed matter via self-diffusion, and suggests its possible application to isotope separation, crystalline control and matter dynamics in massive star.

1) The sedimentation of isotope was achieved on monoatomic Se under a strong gravitational field.

2) In the solid phase experiment, the graded isotopes of $^{82}\text{Se}/^{76}\text{Se}$ of $>0.8$ % was observed in the grown crystalline region.

3) In the solid phase experiment, the graded isotopes of $^{82}\text{Se}/^{76}\text{Se}$ of $>3.5$ % was observed in the almost all region.
Chapter 4, Sedimentation of isotope of Se single element

References

12 The Japan Institute of Metals, Kinzoku Data Book, pp. 23 (Maruzen, Tokyo, 1993).
Fig. 4-1. (a) The polarized microscope photograph of monoatomic Se ultra-centrifuged at $0.92 \times 10^6 G$ in maximum for 100 hours at $190^\circ C$ (in solid phase) and (b) the isotope compositional ratio $^{78}$Se/$^{76}$Se by depth profile using SIMS.
Fig. 4-2. The EBSP mapping data for directions parallel and normal to that of gravity (\parallel\text{gravity} and \perp\text{gravity}) at the marked points by a, b, and c in the ultracentrifuged specimen as shown in Fig. 4-1.
Fig. 4-3. The series of calculated concentration profiles for $^{82}\text{Se}/^{76}\text{Se}$ for an ideal gas reference system together with the experimental result in solid.
Fig. 4-4. The polarized microscope photograph of monoatomic Se ultra-centrifuged at 0.84 x10^6G in maximum for 100 hours at 300℃(in liquid phase). And the isotope compositional ratio $^{82}\text{Se}/^{76}\text{Se}$ by depth profile using SIMS.
Fig. 4-5. the SEM photograph and EBSP mapping data for directions parallel and normal to that of gravity (∥gravity and ⊥ gravity) at the marked rectangular region in Fig. 4-4.
Fig. 4-6. The series of calculated concentration profiles for $^{82}\text{Se}/^{76}\text{Se}$ for an ideal gas reference system together with the experimental result in liquid.
Chapter 5

Sedimentation of Impurity Ge into InSb semiconductor

(Aim for sedimentation of atom and Impurity control)
Chapter 5, Sedimentation of impurity Ge into InSb semiconductor

5-1. Introduction

Materials science research using strong gravitational field up to 1 million G (1 G = 9.8 m/s²) is still an unexploited area. Under strong gravitational field, each atom is displaced by a one-dimensional body force. A strong gravitational field also realized the sedimentation of atoms in solid, i.e. an atomic-scale graded structure, and so on [1,2].

Using ultracentrifugal apparatuses [3,4], we atomic-scale graded structures were previously formed in Bi-Sb alloy [5,6] and In-Pb alloy [7] and Se-Te semiconductor [8] by the sedimentation of substitutional solute atoms, and it enable us to concentrate even isotopes [9,10]. In addition, we observed the grain refinement and the unique deformation twinning under strong gravitational field [11]. In this study, we performed the ultracentrifugal experiment to examine the control of impurity by the sedimentation of atoms from interfacial deposited thin films.

5-2. Properties of In-Sb

We chose the non-dope InSb single crystal (100) for substrate. This material is an n-type and narrow-gap semiconductor (about 0.17 eV) with the zinc-blende crystal structure. Non-dope and n-type InSb(100) wafer was provided by GIRMET Ltd, (Russia), and initial carrier density, electron mobility, etch pit density are (3~7)x10¹⁴ /cm³ at 77K, >4x10⁵ cm²/V·sec at 77K, <200 /cm², respectively.
5-3. Experimental procedure

5-3-1. Sample preparation

InSb wafer was cut off to 3 mm x 3 mm x 450 µm³ for the experiment, and thin impurity atomic film was prepared using Physical Vapor Deposition (PVD which is shown as Figure 5-1) on the polished surface. The thickness of deposited film was about 1 µm. Deposition rate of Ge, Zn, Mn was 0.3~0.5nm/sec and substrate temperature was 100°C. These samples were put into the experimental capsules with sapphire substrate, as shown in Figure. 5-2-a. The impurity elements of experiment were chosen Ge, Zn and Mn. The reasons choice Ge, Zn and Mn were chosen as to make p-type or p-n junction semiconductor, n-type which have career concentration lager, and diluted magnetic semiconductor [12,13,14,15]. We put the deposited surface side to the direction of gravity, because the atomic weight of impurity atoms were smaller than In and Sb.

The air turbine motor type centrifuge [4] was used for this report. We used two-types of sample capsules of Rod-type and Plate-type made of SUS304. We used only Plate-type one in this study. The sample in this capsule receives uniform force and is caused rarely the plastic deformation due to the symmetry shape. The starting samples were set into the capsules and were fixed into a Ti alloy rotor, as shown in Figure. 5-2-b. To compare with usual thermal diffusion, we performed also the annealing experiment at 1 G, using same assembly, at the same temperature and time duration under the same pressure reduction.
5-3-2. Measurement method

The centrifuged samples were evaluated some measurement method. The composition analysis was carried out using an Electron Probe Micro Analyzer (EPMA), JXA-8900 (Japan Electron Optics Laboratories Co., Ltd.). The impurity analysis was carried out using a Secondary-Ion Mass Spectrometer (SIMS), ims-6f (Cameca). Hall effect measurement was carried out using hand made equipment by Van der Pauw measurement at Nakamura Laboratory, department of computer science and electrical engineering, Kumamoto University. Van der Pauw measurement would be explained at next section, particularly.

5-3-3. Hall effect measurement (Van der Pauw method)

Van der Pauw measurement is used often for the evaluation of thin film semiconductor. Figure 5-3 shows Van der Pauw measurement scheme. Voltage of c to d (V_{cd}) was generated when current was loaded a to b (I_{ab}). And V_{da} was generated by I_{bc}.

In this case, we can make equations

$$R_{ab,cd} = \frac{V_{cd}}{I_{ab}}, \quad R_{ab,cd} = \frac{V_{cd}}{I_{ab}}$$

And resistivity $\rho$ is written below equation

$$\rho = \frac{\pi t}{2 \ln 2} \left( R_{ab,cd} + R_{bc,da} \right) f \left( R_{ab,cd} / R_{bc,da} \right)$$  \hspace{1cm} \cdots (1)

$f$ is correction term of sample shape, and calculate by regression from equation

$$\cosh(\frac{r-1}{r+1} \cdot \frac{\ln 2}{f(r)}) = \frac{1}{2} \exp \left( \frac{\ln 2}{f(r)} \right)$$  \hspace{1cm} \cdots (2)

We can use approximation formula (2).

And equation of Hall coefficient $R_H$ is written by

$$R_H = \frac{t}{H} \Delta R_{bd,ac}$$  \hspace{1cm} \cdots (3)

$$\Delta R_{bd,ac} = \left| \frac{V_{ac} - V_{ac,0}}{I_{bd}} \right|$$  \hspace{1cm} \cdots (4)
Chapter 5, Sedimentation of impurity Ge into InSb semiconductor

$V_{ac0}$ is without magnetic field.

Mobility $\mu_H$ is multiplication of $R_H$ and $\sigma$ (conductivity),

$$\mu_H = R_H \sigma = \frac{R_H}{\rho} \quad \cdots(5)$$

Using equation of (1) and (3) finally $\mu_H$ is written by

$$\mu_H = \frac{t}{H \rho} \cdot \frac{\Delta V_{ac}}{I_{dB}} \quad \cdots(6)$$

Career density “n” is written by

$$n = \frac{H}{qt} \cdot \frac{I_{dB}}{\Delta V_{ac}} \quad \cdots(7)$$
5-4 Results and discussion

5-4-1. Centrifuge with Ge impurity thin film

For starting sample, Figure 5-4-a shows the EPMA result of the polished cross section of starting sample of InSb with deposited Ge thin film by PVD. The bulk InSb and Ge thin film was observed. But Ge thin film was peeled off a little, it may be caused by small particles of polisher.

For annealed sample, Figure 5-4-b shows the EPMA result of the polished cross section annealed sample of InSb with deposited Ge thin film by PVD. Annealing was performed at 400°C for 60 hours under pressure reduction and same sample assembly (refer with Fig 5-1). The thickness of Ge film decreased. This indicated that thermal diffusion occurred by terrestrial annealing.

And for ultracentrifuged sample, Figure 5-4-c shows the EPMA result of the polished cross section of the ultracentrifuged sample. The ultracentrifugal conditions were about $0.59 \times 10^6$ G in maximum and at 400°C for 60 hours under the pressure reduction for several tens Pa.

The concentration of Ge on thin film decreased, while the thickness did not change much in comparison with the starting sample. To clarify the composition depth profile, we performed the composition analysis of $^{74}$Ge of the annealed sample and the ultracentrifuged one by SIMS as shown Figure. 5-5. Y axis and X axis of Fig. 5-4 is calibrated intensity (arbitral unit) and depth converted from time to length by confocal laser scanning microscopy from deposition surface, respectively. The depth profile of the annealed sample was steep and shallow at the near of the deposited surface. On the other hand, one of the ultracentrifuged sample was gently, and deeper. As a result, the diffusion depth of ultracentrifuged sample was estimated to be 4 times deeper than annealed one at the threshold value about $10^2$ cps.
5.4.2. Centrifuge with impurity thin film of transition metals (Zn and Mn)

For starting sample, Zn and Mn thin film as deposit on InSb, we could not observe by EPMA measurement. Melting point of Zn and Mn are too low and too high, in this reason, it is difficult to make strongly jointed film and it is easily peeled off by polished process.

Figure 5-6-a) and 5-6-b) shows the EPMA result of the polished cross section of 60 hours annealed starting sample which is InSb with deposited Zn and Mn thin film by PVD. Annealing was performed 60 hours under decompression of several tens Pa and same sample assembly. In the case of Zn on InSb, we could not observe the Zn thin film. It may be thought that it is caused by surface migration. In the case of Mn on InSb, we could observe the Mn decomposition at the small void.

Figure 5-6-c) and 5-6-d) shows the EPMA result of the polished cross section of 60 hours centrifuged sample which is InSb with deposited Zn and Mn thin film by PVD. The conditions of the gravitational experiment in this study were about $0.59 \times 10^6$ G in maximum and at 400°C, and the duration was 60 hours under decompression of several tens Pa. In the case of Zn on InSb, multi layer phase and Zn decomposition with Kirkendall void and the periodic chemical diffusion could be observed. T. C. Chou discussed about similar periodic diffusion between SiC and Pt, he mentioned it may be caused by Gibbs energy of ternary phase diagram [17].

In the case of Mn on InSb, we could observe the Mn decomposition with Kirkendall void and highly diffusion of Indium to opposite gravitational direction which likes disappearance, in spite of In is heavier than Mn. We consider that it may be caused by electronegativity. But both case of Zn and Mn were observed centrifuged specimens.
5-4-3. Centrifuge pure InSb single crystal

We examined ultracentrifuged experiment for InSn single crystal with no impurity element film. The ultracentrifugal conditions were about $0.38 \times 10^6$ G in maximum and at $350^\circ$C for 50 hours under the pressure reduction for several tens Pa. Sample, Figure 5-7 and Table 5-1 shows the electrical properties measurement result of Van der Pauw measurement.

We measured standard sample, annealed at $400^\circ$C for 60 hours under 40 Pa, and centrifuged sample. Y axis and X axis of Fig. 5-7 is electron mobility (cm$^2$/V·s) and carrier density (cm$^3$), respectively. In the case of standard sample and annealed sample, each value of electric properties was almost same, resistivity was $0.45 \times 10^{-3}$ Ω·cm, electron mobility was $5.9 \times 10^4$ cm$^2$/V·sec, and career density was $2.3 \times 10^{16}$ cm$^{-3}$. But, in the case of centrifuged sample, resistivity was $0.49 \times 10^{-3}$ Ω·cm, electron mobility was $2.8 \times 10^4$ cm$^2$/V·sec, and career density was $4.4 \times 10^{16}$ cm$^{-3}$.

As a results, the career density, electron mobility and resistibility of centrifuged sample change to 2times, a half, 10% increasing, respectively. We assume that increasing of the defect (which like point defect) cause the change of these electron properties due to the centrifugal treatment.
5-5 Summary

We performed the ultracentrifugal experiment to examine the control of impurity by the sedimentation of atoms. In the case of Ge impurity element, we could observe the larger concentration change than usual thermal diffusion. The diffusion under strong gravitational field (the sedimentation) is powerful and directional. But, in the case of transition impurity element, we could observe chemically and periodic diffusion. But these were different reactions comparing gravitational diffusion with thermal diffusion, drastically.

And career density was changed two times than initial and annealed sample in InSb single crystal without any impurity thin film. And we can mention that it is caused by the increasing of defect and change of defect level in semiconductor.

1) In the case of Ge impurity element into InSb substrate, the concentration change was observed 4 times larger than usual thermal diffusion.
2) In the case of transition metals impurity element into InSb substrate, the periodic diffusion and the chemical diffusion was observed.
3) In the case of pure InSb centrifugal treatment, the increase of career density was observed due to the change of defect level.
Chapter 5, Sedimentation of impurity Ge into InSb semiconductor

References

Table 5-1 Resistivity of initial one, annealed one and centrifugal treated one.

<table>
<thead>
<tr>
<th>resistivity</th>
<th>standard</th>
<th>annealed STD</th>
<th>centrifuged</th>
</tr>
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<tr>
<td>$\rho$ [Ω cm]</td>
<td>4.540E-03</td>
<td>4.589E-03</td>
<td>4.948E-03</td>
</tr>
</tbody>
</table>
Chapter 5, Sedimentation of impurity Ge into InSb semiconductor

Figure 5-1. Photograph of resistance heating PVD apparatus and its scheme of cross section.
Figure 5-2. (a) Photographs and assembly of experimental sample and cross section of it with capsule and (b) cross section of rotor and sample in which the left capsule is Rod type and right is Plate type.
Figure 5-3. Schematic picture of Van der Pauw method
Figure 5.4. (a) EPMA mappings of Ge as deposited on InSb (b) EPMA mappings of annealed InSb sample with deposited Ge for 60 hours (c) EPMA mappings of ultracentrifuged InSb sample with deposited Ge. (60 hours, 400°C, and 0.59×10^6 G)
Figure 5-5. SIMS analysis of $^{74}$Ge depth profile of ultracentrifuged sample and annealed one.
Chapter 5, Sedimentation of impurity Ge into InSb semiconductor

Zn element cannot be found.

Figure 5-6. Result of EPMA mapping analysis of annealed starting sample which was performed 60 hours under decompression of several tens Pa and same sample assembly. a) annealed InSb with deposited Zn, b) annealed InSb with deposited Mn, and centrifuged sample which was performed 60 hours at 400°C and $0.59 \times 10^6$ G in maximum under decompression of several tens Pa c) experimented InSb with deposited Zn, d) experimented InSb with deposited Mn.
Figure 5-7. Results of resistivity and hall effect using Four-Point Probe Method on InSb single crystal ultracentrifued at about $0.38 \times 10^6$ G in maximum and at $350^\circ$C for 50 hours
Chapter 6

Interface structure control of a-Si:Ge multi layer thin film
(Aim for Control of Interface)
Chapter 6, Interface structure control of a-Si:Ge multi layer thin film

6-1. Introduction

Research of interfacial morphology is very important at any field, for examples, devices of semiconductor, Giant Magnetic resistance and etc... but there is no report of the interfacial morphology using gravitational field. We assume that a strong gravity (It is equal to say atomic mass differences) induced diffusion is very effective for control of interfacial morphology. And Zoltan Erdelyi et al. who is Dept. of solid state physics, Debrecen University, in Hungary, they reported the interface sharpening only annealing treatment [1]. They found that the sharper interface is obtained initially smeared composition interface in Mo/V multi layer system. And we try to more sharpening using a gravitational treatment, additionally. This research is cooperative research of Kumamoto University and Debrecen University.

6-2. Preparation of a-Si:Ge multi thin film

Amorphous Si and amorphous Ge multi layer thin film was prepared by Prof. Gábor Langer, department of solid state physics, Debrecen University, Hungary, using magnetron sputtering [2] on Si substrate. The conditions were 5x10⁻³ mbar in Ar, deposition rate of a-Si is 0.1nm/sec and a-Ge is 0.5nm/sec and these deposition rates were measured by a quartz oscillator. Samples were prepared 4types; these were initially sharp interface for thick bilayer and thin bilayer, and initially smeared interface for thick bilayer and thin bilayer. Figure 6-1 and Table. 6-1 shows samples which we experimented.

Magnetron sputtering deposition method is good for making the epitaxial like high oriented thin films compare with general PVD method. For these experiments, the grain boundary is not good for observation of volume diffusion. So we have to prepare the single crystal thin film, usually, but a-Si:Ge system is very difficult to make single crystal thin film, and then we choose the sample assembly using the amorphous system. And we investigated the effect of interface morphology under strong gravitational field.
6-3. Experimental procedure

To compare with as deposit one, annealed one and gravity treated one; we performed a strong gravitational experiment (380,000 G, 400°C, 60 hours in Ar gas) and annealing experiment (400°C, 64 hours in Ar gas). Figure 6-2 shows the assembly of centrifugal experiment, and sealed in Ar gas in the glove box. After these experiment, thinner samples (I, II) were evaluated by Small Angle incident X-ray measurement by X-ray diffractometer (Siemens), as shown Figure. 6-3-a.

And we compare the SAX diffract patterns with simulation of IMD [3,4] made by ESRF. Small Angle X-ray reflection (2theta is about less than 10°, usually) measurement give us the information of thin film structure.

IMD can be used for both modeling and for parameter estimation by nonlinear, least-squares curve-fitting (including confidence interval generation). They can simulate using Fourier Transformation of electron density and polarizations. They computed using an algorithm that is based on recursive application of the Fresnel equations [5], modified to include interfacial roughness and/or diffuseness [6,7]. Non-specular reflected intensities can be computed using either a dynamical Born approximation vector theory [8], or the so-called ‘Distorted-Wave Born Approximation’ formalism [9-12], a scalar theory which is nonetheless valid below the critical angle of total external reflection in the X-ray region. For both specular and non-specular computations, a stochastic model of film growth and erosion [13] can be used to account for the evolution of interfacial roughness through the film stack. Alternatively, a more conventional roughness model [14] can be used, with the option of defining depth-graded roughness and correlation length parameters.

Thicker samples were measured by Secondary Neutron Mass Spectroscope (INA-X (SPECS GmbH, Berlin)) to investigate interface profile and thickness of bilayers, as shown Figure. 6-3-b.

This “SNMS” technique is similar to SIMS and is also known as “Sputtered Neutral Mass Spectrometry”. In this method the neutral atoms are sputtered from a sample surface by the help of the Ar, Kr, Ne, etc. plasma and detected after a post-ionization. The post-ionization can be performed by a laser light or Electron Cyclotron Wave Resonance (ECWR) plasma. The main part of sputtered particles is in neutral state (near 99 %), so the quantitative estimation by SNMS is much better than by SIMS.

Secondary Neutral Mass Spectrometry (SNMS) is a suitable technique to
Chapter 6, Interface structure control of a-Si:Ge multi layer thin film

Measure the chemical composition of almost any sample, because the flux of atoms sputtered from the sample is representative of the stoichiometry of the top-most layer. This is in contrast to X-ray Photoelectron Spectroscopy (XPS) systems combined with an ion gun, where preferential sputtering makes analysis more difficult. Further advantage of SNMS is its applicability to insulators, which causes serious problems in methods, which rely on electron emission or excitation by a primary beam of electrons, (such as Auger Electron Spectroscopy, AES or XPS).

In SNMS, the sample is bombarded with rare gas ions with energy in the range of 0.5 to 5.0 keV. This leads to the sputtering of atoms and molecules from the sample, which leave the surface.

The flux of sputtered particles consists of ions and neutral atoms. The neutral atoms are detected by post-ionizing the atoms that are ejected from the surface. The probability to sputter ionized atoms from a surface can vary from $10^{-5}$ to $10^{-1}$ and depends strongly on the surface composition (matrix effect). The majorities of sputtered particles are neutral and thus only vary between 90% and 99.9999%. This smaller sensitivity to the surface composition reduces matrix effect and allows a much better quantitative estimate of the stoichiometry.

In this SNMS measurement acceleration voltage was 300 eV, and clearance between plasma and sample was 2.5 mm, and we used Kr gas for plasma.

These equipments were laboratory of Prof. Dezső Beke, department of solid state physics, Debrecen University and Institute of Nuclear Research of the Hungarian Academy of Sciences in Hungary.
Chapter 6, Interface structure control of a-Si:Ge multi layer thin film

6-4 Results and discussion
6-4-1. SAX (Small angle incident X-ray) measurement

The thickness profiles of multi thin layer were confirmed by Small Angle incident X-ray diffraction (reflectance). Figure 6-4 shows SAXRD results for sample I (thin and initially sharp interface). In this result, the diffraction peak was observed at around 1.1° (1st peak) in all samples. This peak show that the thickness of one bilayer which is 8 nm. And the diffraction peak at 2.5° (3rd peak) was observed only as deposited sample, this peak shows the thickness of 4 nm which is thickness of each rayer of Si and Ge. 3rd peak of heated sample at 1G and centrifuged was disappeared to compare with as deposit one. But, any other differences of thickness and interface morphology in heated sample at 1G and centrifuged were not observed. These indicate the symmetrical interface structure on as deposit sample. But annealed one and centrifuged one change the interface structure. The disappearance of 3rd peak was explained by diffused interface composition morphology due to the annealing.

Figure 6-5 shows SAXRD results for sample II (thin and initially smeared interface). In this result, all of diffraction pattern has 1st peak which is around 1.1°, this degree indicate the thickness of one bilayer, too. But in the case of thin and initially smeared sample, we could observe the 2nd peak in centrifuged sample, only. This result indicate the something change of interface structure.

To confirm the interface morphology, SAX diffraction patterns in some case were simulated. Figures 6-6-a), 6-6-b), 6-6-c) show the simulation result by IMD. Interface models were made for simulations as shown in figure 6-6-a'), 6-6-b'), 6-6-c'). Simulation results of Fig. 6-6-a), 6-6-b), 6-6-c) are corresponding to interface and composition structures of Fig. 6-6-a'), 6-6-b'), 6-6-c'). Then, the Fourier transform of the electron density was required and diffraction patterns were simulated based on the refractive and diffraction.

These simulation results of x axis is θ, x axis of experimental data is 2θ, and y-axis is intensity. This intensity strength depends on the layer thickness and the interface sharpness (the refractive index).

As a result, the 2nd peak was only observed in the case of asymmetry interface structure as shown Fig 6-6-c). This diffraction pattern is very similar with centrifuged sample II (thin and initially smeared interface) as shown Fig. 6-5-c).

Considering these results, the asymmetry interface structure was archived in the gravity treated sample which has initially smeared interface and it can be say
that the interface sharpening effect is larger and interface morphology can be controlled if we applied under a strong gravitational field and
6-4-2. SNMS (Secondary Neutron Mass Spectroscope) measurement

Figure 6-7 and Figure 6-8 show the SNMS results of sample III (thick and initially sharp interface) and sample IV (thick and initially smeared interface), respectively. Measurement conditions were 300 eV for acceleration voltage and 2.5 mm for clearance between plasma and sample.

Each x-axis is sputtering time and y-axis is intensity. And we try to convert from raw data to quantitative data only as deposit and annealed sample III (thick and initially sharp interface), but we could not get good results as shown Fig 6-7. It is difficult to measure the depth profile due to the equipment and sample problems.

In the case of sample IV (thick and initially smeared interface), all of measurement data were bad. We could not determine the intensity of Si and Ge, because of Ge is very difficult to sputter by Neutron particle. So before we sputtered Ge layer, we can observe the Si intensities sputtered by Neutron particles. It is remarkable in the sample which has smeared interface.

Especially, centrifuged sample had the problems that it was coated by Carbon layer due to use the organic abrasive, so impossible to measure the depth profile. To solve these problems, we thought that this sample system have to be changed.
Summary

We performed a strong gravitational experiment and annealing treatment, and then we investigate the interface morphology using X-ray diffraction and SNMS. The X-ray measurement indicates the achievement of asymmetry interface morphology and more sharpening by under a strong gravitational field. But we still have the problems for experimental method, sample preparation and selection of sample. However, we can certificate that it is possible to control of interface structure using a strong gravitational field.

1) The asymmetry interface was indicated on centrifuged sample II (thin and initially smeared interface) by SAX measurement and simulation.
2) SNMS measurement results were bad due to the difficulty of detection of Si, Ge and the centrifuged sample problems.
References

3 David L. Windt, X ray Oriented Programs, IMD2.11
   http://www.esrf.eu/computing/scientific/xop2.1/extensions.html#IMD
Table 6.1 Summary of experimental samples.

<table>
<thead>
<tr>
<th></th>
<th>Bilayer</th>
<th>Thickness</th>
<th>Interface Type</th>
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<tr>
<td>I</td>
<td>25bilayer</td>
<td>8nm thickness</td>
<td>sharp interface</td>
</tr>
<tr>
<td>II</td>
<td>25bilayer</td>
<td>8nm thickness</td>
<td>smeared interface</td>
</tr>
<tr>
<td>III</td>
<td>3bilayer</td>
<td>20nm thickness</td>
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<tr>
<td>VI</td>
<td>3bilayer</td>
<td>20nm thickness</td>
<td>smeared interface</td>
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Figure 6-1. Experimental samples for centrifugal experiment.
(I) initially sharp interface and thickness of one bilayer is 8nm and 25 bilayers
(II) initially smeared interface and thickness of one bilayer is 8nm and 25 bilayers
(III) initially sharp interface and thickness of one bilayer is 20nm and 3 bilayers
(IV) initially sharp interface and thickness of one bilayer is 20nm and 3 bilayers.
Figure 6-2. The scheme and photographs of experimental assembly and cross section of it with capsule
Figure 6-3. a) X-ray diffractometer (Siemens) apparatus in Debrecen University and b) SNMS equipment in Debrecen University (INA-X (SPECS GmbH, Berlin)).
Figure 6-4. SAXRD results for sample I (thin and initially sharp interface) of as deposit, annealed one in Ar, and centrifuged one at 0.38x10^6 G
Chapter 6, Interface structure control of a-Si:Ge multi layer thin film

Figure 6-5. SAXRD results for sample II (thin and initially smeared interface) of as deposit, annealed one in Ar, and centrifuged one at 0.38x10⁶ G.
Figure 6-6. Results of simulation for SAXRD for each condition as shown Right side graph which indicate the composition and interface profiles.
Figure 6.7. Depth profiles for sample III (thick and initially sharp interface) of as deposit, annealed one in Ar, and centrifuged one at 0.38x10^6 G by using SNMS measurement.
Figure 6-8. Depth profiles for sample III (thick and initially sharp interface) of as deposit, annealed one in Ar, and centrifuged one at 0.38x10^6 G by using SNMS measurement.
Chapter 7

Conclusion
7-1. Summary of this dissertation

In this study, we studied the next step researches from sedimentation of atoms, application and more principle phenomena of what happen in a strong gravitational field. We can make clear the some effect and mechanism, for example, there are many defect, lattice strain, repeatable nucleation and others. But, all of mechanism and phenomena has still unknown.

In the Chapter 1, we introduced ultracentrifugal field, expected effect on materials and some previous works.

In the Chapter 2, we introduced the development and setup of new ultracentrifuge and arranged the specification of the ultracentrifuge for our experiment.

In the Chapter 3, we performed the ultracentrifuged experiment on the Bi-Sb alloy. We found that deformation twins appear in the low-gravity region where grain refinement is not observed. Compared with conventional deformation twins, these twins were much thicker and were proportional to the gravitational field. For grain refinement, the minimum gravitational field was more than 0.17×10^6 G, at 240 °C for periods <10 hours. Deformation twinning which formed under a strong gravitational field has only one kind of slip plane because of a one dimensional body force.

In the Chapter 4, we performed the ultracentrifuged experiment on the monoatomic Se, and the enrichment of isotope was achieved. In the solid state experiment, at 0.8-1 million G and at 190°C. Change in concentration ratio ^82Se/^76Se of >0.8 % was observed in the grown crystalline region. These results show an evidence for sedimentation of substitutional atoms in solid via self-diffusion. In the liquid state experiment, the concentration ratio ^82Se/^76Se increased by greater than 3.5 % in specimen ultracentrifuged at 0.7-0.9 million G and at 300°C. The recovered sample had a feather-shaped crystalline morphology. The concentration gradient was nearly twice that of the steady state analytical result (ideal gas system), indicating a non-ideal system diffusion.

In the Chapter 5, we performed the ultracentrifuged experiment on the single crystal InSb, and larger diffusion of impurity element was achieved. The diffusion under strong gravitational field (the sedimentation) is powerful and directional. And career density was changed larger than initial and annealed sample in InSb single crystal without any impurity thin film. It is expected by the
increasing of defect and change of defect level in semiconductor.

In the Chapter 6, we performed the ultracentrifuged experiment on the a-Si:Ge multi thin film sample. The asymmetry and sharper interface morphology was obtained. We investigate the interface morphology using X ray diffraction and SNMS in Hungary. X ray measurement shows the achievement of asymmetry interface morphology and more sharpening by under a strong gravitational field. We can certificate that it is possible to control of interface morphology using a strong gravitational field.
Acknowledgements

The author would like to be grateful to Prof. Mashimo of Kumamoto University for his guidance, support, and encouragements consistently in carrying out this PhD dissertation.

And the author would like to be grateful to Dr. M. Ono, Dr. S. Okayasu of Advanced Science Research Center, in JAEA and Prof. A. Yoshiasa of department of science, Prof. M. Matsuda and Y. Morizono of department of material engineering Prof. C. Iwamoto of department of mechanical engineering, Prof. Y. Nakamura of department of electrical engineering in Kumamoto University and Dr. T. Sano in Osaka University and Dr. X. Huang of Advanced Industrial Science and Technology and Dr. T. Kinoshita of Toyama Prefectural University, for their helpful discussion and experiments.

Especially, the author would like to say staffs of department of solid state physics, Debrecen University in Hungary, Prof. Dezső Beke, Dr. Zoltán Erdélyi, Dr. Attila Csík, Dr. Gábor Langer, Dr. Kálmán Vad, Mr. Ákos Lakatos and many people who helped my international internship and my research activities for 2months.

And for our Gravity Group, I would like to say the gratitude to Miss. R. Bagun, Mr. Ogata, Mr. Kondo, Mr. Sakata, Mr. Shimowaki and Mr. Yasuyuki Abe(in Ihara Lab), and other laboratory mate in 2009, Dr. Emil, Mr. Chen, Mr. Lee, Mr. Tashiro, Mr. Murai, Mr. Shimokawa, Mr. Gomoto, Mr. Ata Mr. Takashima and Mr. Taniguchi.

This work was supported in part by the 21th Global COE program of Pulsed Power Science and grant Aid for Scientific Research from Japan Ministry of Education, Science, and Culture.